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Development and optimization of headspace and headspace-solid phase microextraction for the determination of volatile fuel compounds in environmental samples

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Desarrollo y optimización de métodos de extracción en headspace y microextracción en fase sólida en headspace para la determinación de compuestos volátiles de combustibles en muestras medioambientales

Desenvolvimento e optimização da extração headspace e microextração headspace em fase sólida para determinação de compostos voláteis de combustíveis em amostras ambientais

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ABSTRACT

The application of an effective and sensitive analytical method to determine soil contaminants is a crucial step in monitoring and remediation processes. In the present work, we optimized the analysis of volatile organic compounds (VFOC) commonly present in fuel: oxygenates (FO-MTBE and ETBE-) and monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene (BTEX). Headspace (HS) and headspace-solid phase microextraction (HS-SPME) were optimized in water samples, and validated for contaminated soils, using artificially spiked soils. Contaminants were identified and quantified by gas chromatography coupled to mass spectrometry (GC/MS). Matrix effect correction with surrogate standards resulted essential when analyzing soil samples, especially when the sample exerted a strong sorption on the contaminants.

RESUMEN

La aplicación de metodologías analíticas sensibles y efectivas para la determinación de los contaminantes del suelo es una etapa crucial para la realización de experimentos de monitorización y remediación. En el presente trabajo, se optimizó el análisis de compuestos orgánicos volátiles (VFOC) comúnmente presentes en combustibles: incluyendo compuestos oxigenados (FO-MTBE y ETBE-) e hidrocarburos monoaromáticos, tales como benceno, tolueno, etilbenceno y xileno (BTEX). Los métodos de extracción en headspace (HS) y microextracción en fase sólida en headspace (HS-SPME) fueron optimizados para aguas contaminadas y después validadas para suelos, utilizando muestras contaminadas de forma artificial. La corrección del efecto matriz con estándares tipo surrogate fue esencial para el análisis de muestras de suelos, especialmente para aquellas que ejercían una fuerte adsorción sobre los contaminantes.

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RESUMO

A aplicação de um método analítico eficaz e sensível para determinar contaminantes orgânicos do solo e da água é um passo essencial durante os processos de monitorização e recuperação ambiental. No presente trabalho optimizou-se a análise de alguns compostos orgânicos voláteis que surgem, usualmente, nos combustíveis: compostos oxigenados (FO- MTBE e ETBE-) e hidrocarbonetos monoaromáticos tais como benzeno, tolueno, etilbenzeno e xileno (BTEX). As metodologias de extracção headspace (HS) e microextracção em fase sólida em modo headspace (HS-SPME) foram otimizadas em amostras de água e validadas para amostras de diferentes solos contaminados artificialmente. Os contaminantes orgânicos foram identificados e quantificados por cromatografia gasosa associada a espectrometria de massa (GC/MS). A correção do efeito da matriz com padrões surrogate foi essencial para a análise das amostras de solo, especialmente em solos que apresentavam uma forte adsorção dos contaminantes.

KEY WORDS
Volatile organic compounds, HS, HS-SPME, water and soil samples.

PALABRAS CLAVE
Compuestos orgánicos volátiles, HS, HS-SPME, muestras de aguas y suelos.

PALAVRAS-CHAVE
Compostos orgânicos voláteis, HS, HS-SPME, amostras de água e solo.

1. Introduction

Applying an appropriate and effective analytical method for the determination of volatile fuel organic compounds (VFOC), (benzene, toluene, ethylbenzene and xylene –BTEX- and fuel oxygenates -FO-) in environmental samples, is the basis for carrying out solid sorption, monitorization and/or remediation studies.

The most commonly used technique to analyze volatile compounds in soils is equilibrium headspace analysis (HS) coupled to gas chromatography/mass spectrometry (GC/MS) (Esteve-Turrillas et al. 2007; Pavón et al. 2009; García Pinto et al. 2011). The HS procedure has the advantage that very little sample manipulation is required, which minimizes the loss of contaminant. Furthermore, this method saves an enormous amount of time, and does not use organic solvents, as other extraction techniques for organic contaminants. As an alternative, head space-solid phase microextraction (HS-SPME) has been used for VFOC analysis in diverse environmental matrices (Llompart et al. 1999; Arambarri et al. 2004; Ezquerro et al. 2004). This technique was developed in the 1990s by Prof. Pawliszyn's research group (Arthur and Pawliszyn 1990; Louch et al. 1992; Zhang and Pawliszyn 1993). This technique uses selective fibers, consisting of a fused silica rod covered with a polymeric coating. HS-SPME combines the advantages of HS extraction and the concentration in a single step (Zhang and Pawliszyn 1993).

The principal limitation of HS and HS-SPME analysis is the matrix effect in solid samples; i.e. samples with different properties would exert dissimilar degrees of sorption, modifying the analytical recovery. This matrix effect can be minimized by using surrogates, compounds with similar properties to the analytes but rarely found in environmental samples. They should be spiked to the samples and standards in a constant concentration and stabilized for a proper amount of time to be sorbed by the sample in a similar extent than analytes, so that this matrix effect can be corrected (Rosell et al. 2006; Hiatt 2010).

The aim of the present article was to optimize the extraction and analysis of VFOC (FO and BTEX) in water and soil samples, using HS and HS-SPME with GC/MS quantification.

2. Materials and methods

2.1. Reagents and standards

The following reagents were used: benzene (purity, 99.8%; grade, PAI-ACS (UV-IR-94 HPLC-GPC)), toluene (purity, 99.8%; grade, PAI-ACS (UV-IR-HPLC-GPC)), ethylbenzene (purity, 99%; grade, PS), *o*-xylene (purity, 99%; grade, PA (Reag.USP. Ph. Eur)), *m*-xylene (purity, 99%; grade, PA (Reag. Ph. Eur)), *p*-xylene (purity, 99%; grade, PA (Reag. USP)), MTBE (purity, 99.7%; grade, PAI (PAR)) and ETBE (purity, 99%; grade, PA (Reag. USP)). Fluorobenzene (purity, 99%) was used as surrogate. All reagents were purchased from Panreac Química, S.L.U., except fluorobenzene, purchased from Sigma-Aldrich Co, LLC. Standard solutions, one of FO and BTEX and another of fluorobenzene, were prepared in methanol (purity, 99.9%; grade, PAI (PAR)), with each of the reagents at a concentration of 100 mg L^{-1}. These solutions were used for the preparation of standards and for soil and water spiking.

2.2. Preparation of water and soil samples

Spiked distilled water standards of 500 µg L^{-1} of individual FO (MTBE and ETBE) and BTEX (benzene, toluene, ethylbenzene and xylene) were used for HS and HS-SPME optimization. 2 mL of distilled water and 10 µL of standard solution were added in 22-mL volatile organic analysis (VOA) vials and hermetically closed and homogenised before analyzing.

Samples of the A and B horizon (A_{Camb} and B_{Camb}) from an alumi-umbric Cambisol profile collected in the surroundings of Santiago de Compostela (Galicia, NW Spain) were used. According to USEPA Method 5021A (volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis) (USEPA 2003), the soil was mixed with organic free distilled water to create a slurry. One gram of sample was mixed with 2 mL of distilled water, and the slurry was spiked with the standard solution until 1000 µg kg^{-1} of individual FO and BTEX. The slurry was stabilized in hermetically sealed VOA vials at 4 ºC for 7 days before analyzing.

Calibration standards were prepared with the 100 mg L^{-1} standard in VOA vials with 2 mL of distilled water. For HS, standards of 50 to 15000 µg L^{-1}, and for HS-SPME, of 0.5 to 2500 µg L^{-1} were prepared. Fluorobenzene was added to water standards at constant concentration (2500 µg L^{-1}) to be used as internal standard for calibration. In the case of soil samples, fluorobenzene was added also as surrogate or matrix effect corrector, during the spiking process and stabilized with the rest of the analytes at 4 ºC for at least 7 days. Fluorobenzene concentration was also maintained constant at 5000 µg kg^{-1}.

2.3. Instrumentation and analytical methods

The analysis instrumentation consists of an autosampler (Combi PAL, Agilent Technologies), with liquid, HS and SPME injection and an oven for heating and agitating VOA sample vials, a gas chromatograph (Model 450 GC, Agilent Technologies) and an ion trap mass spectrometer (Model 220 MS, Agilent Technologies). Cycle Composer software (Version 1.5.4; CTC Analytics AG) was used to control the Combi PAL autosampler and MS Workstation software (Version 6.9.3; Varian, Inc.) was used to control the GC-MS system and to process the data.

In HS and HS-SPME, VOA vials containing the samples were heated in the HS oven, with constant agitation and for a suitable period of time to achieve an acceptable equilibrium between the HS and the sample. As presented in **Figure 1a**, when the VOA vial contains an aqueous sample, the equilibrium takes place between the liquid and the headspace of the vial. When there is a soil/water slurry (**Figure 1b**), the equilibrium takes place among three phases (soil, water and headspace) and the interaction of soil with the analytes or sorption, will provoke a lower displacement towards the headspace, compared to water standards, where there are no sorption processes. This is known as matrix effect and should be corrected, as already said, with the addition of a standard surrogate. In HS analysis an aliquot of the HS gas is directly injected into the chromatograph. In HS-SPME, a fiber is introduced in the vial

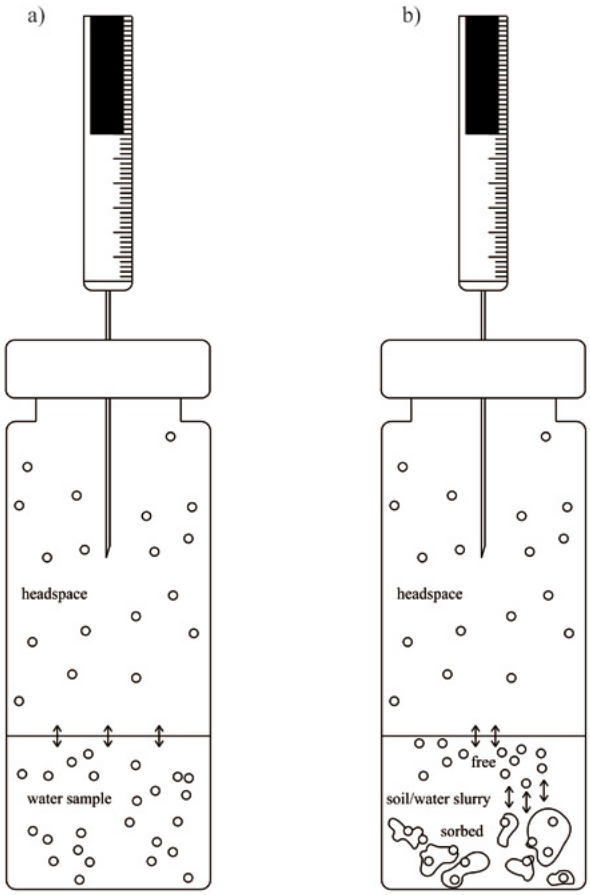

Figure 1. Simplification of equilibrium processes occurring in VOA vials with water (a) and soil (b) samples during HS analysis.

during oven equilibration, to absorb the analytes in the HS. The amount of analyte absorbed is proportional to the concentration in the HS, and therefore to the concentration in the water or soil sample (also with matrix effect correction).

Therefore, after the equilibration time, in direct HS sampling, 1 mL of HS gas was directly injected in the chromatograph for analysis. The injector was operated at 250 ºC and in split 1/10 mode. In the HS-SPME method, a 75 µm Carboxen-PDMS fiber (Supelco) was exposed to the headspace during equilibration and then thermally desorbed for 5 min at 300 ºC (temperature defined by the manufacturer) in the injector, that also operated with a 1/10 split ratio. Before introducing the fiber in the vial, the sample had to stabilize in the HS oven at the incubation temperature for 5 min. After desorption, SPME fibers underwent a bakeout process under N_2 current to clean the remaining traces of contaminants. Usually, the bakeout temperature is fixed 20 ºC under the desorption temperature, in this case 280 ºC.

The chromatographic column used was a FactorFour VF-5ms EZ-Guard (supplied by Agilent Technologies) of 30 m x 0.25 mm x 0.25 µm. The column oven temperature varied as follows: 35 ºC (held for 5 min), 10 ºC min^{-1} up to 80 ºC and 25 ºC min^{-1} up to 200 ºC (held for 0.7 min). The carrier gas was helium with a constant flow of 1 mL min^{-1}. The mass spectrometer operated in full scan mode. *m*- and *p*- xylene were quantified as a single peak.

The analytical performance characteristics were established for HS and HS-SPME-GC-MS

methods using water spiked standards and uncontaminated blanks. Limits of detection (LOD) were calculated as 3.3 times the standard deviation of the blank (*n=10*) divided by the slope of the calibration curve. Limits of quantification (LOQ) were calculated as ten times the standard deviation of the blank (*n=10*) divided by the slope of the calibration curve (García Pinto et al., 2011). The linear range goes from the LOQ to the highest standard until which the calibration curves were linear, with significant R^2 coefficients.

2.4. Optimization of VFOC extraction and analysis

For VFOC (FO and BTEX) analyses in water and soil samples, HS and HS-SPME conditions were optimized. The most important parameters to optimize in a HS process are the extraction temperature and the extraction time, apart from others like the sample size or the agitation speed. HS conditions were varied in the range commonly found in the literature, with the rest of parameters held constant. The extraction temperatures tested were 60, 80 and 90 ºC, for 15 min of extraction time and 500 rpm of agitation speed. Extraction times of 10, 15 and 20 min were used at 80 ºC and 500 rpm. The sample sizes and slurry ratios (1 g:2 mL and 1 g:5 mL) and agitation speeds (500 and 700 rpm) were optimized at 80 ºC and 15 min. The optimum values were selected in order to obtain the highest analytical response of the contaminants. HS-SPME optimum conditions were established based on HS results, and different incubation times were tested (15, 20 and 30 min). HS and HS-SPME-GC-MS methods were optimized with spiked distilled water and then validated for soil analysis with spiked soils with matrix effect correction.

3. Results and discussion

3.1. FO and BTEX HS-GC-MS analysis optimization

3.1.1. Optimization of HS parameters

Several parameters that highly influence the analytical sensitivity of HS analysis were optimized: extraction temperature, extraction time, sample size and agitation speed.

The peak sizes of the individual FO and BTEX obtained for each temperature and extraction time tested are presented in **Figure 2**. The highest peak size was reached at 80 ºC. At 60 ºC the equilibrium concentration was lower, probably due to the lower volatilization of the analytes towards the HS. At 90 ºC, the higher vial temperature provoked a pressure increase. This could also increase the vaporization temperature of the analytes, which could explain the lower volatilization of the HS (**Figure 2a**). The extraction time with the highest peak size was 15 min, although only MTBE, ETBE and benzene showed higher significant differences between 15 min and/or 10 and 20 min (**Figure 2b**). As a result, 80 ºC and 15 min were used as optimum.

According to EPA method 5021A (USEPA 2003), 10 mL of aqueous samples or 2 g of soil samples (or less in case of high concentration) + 10 mL of organic free distilled water should be added to 22-mL VOA vials for HS analysis. By direct observation, the total column of 10 mL was very difficult to agitate homogeneously during HS incubation. Different liquid volumes from 1 to 10 mL were tested to select the volume that allowed better agitation. The best agitation was obtained for 2 mL. In the case of soil, lowering the slurry proportion soil/water to 1 g:2 mL also produced a more homogeneous slurry and was easier to agitate than the recommended EPA Method 5021 (2 g:10 mL or 1 g:5 mL).

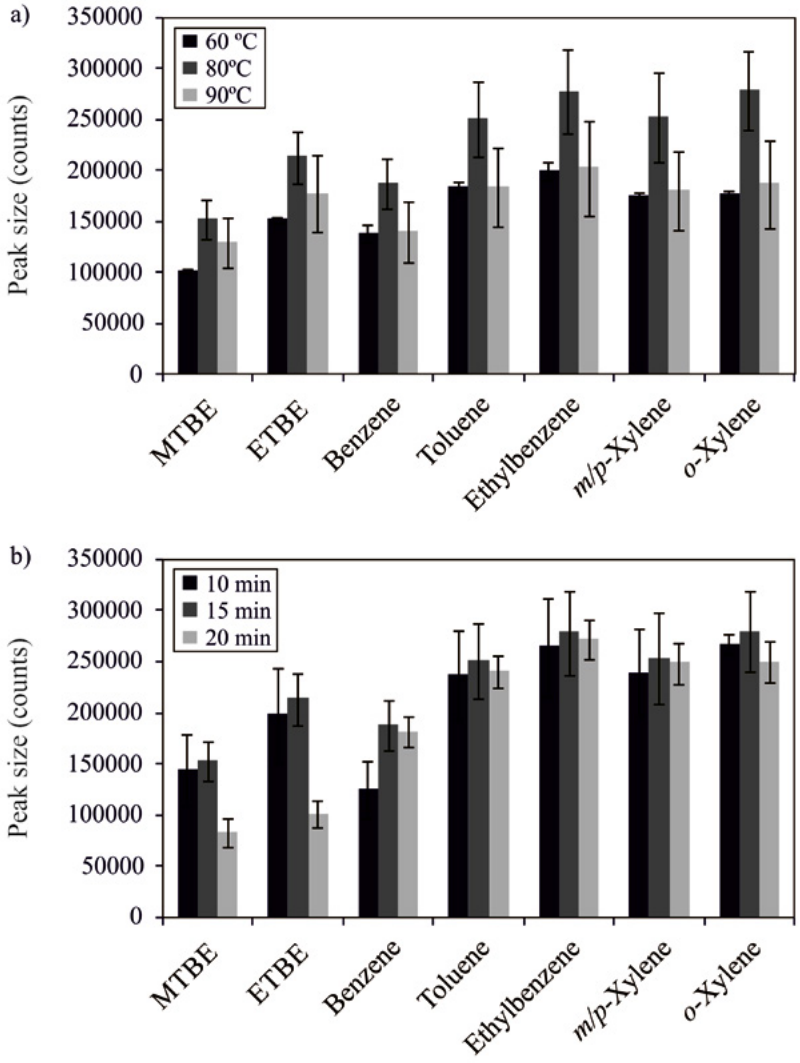

Figure 2. Peak sizes of individual FO and BTEX in 500 µg L^{-1} water standards analyzed by HS-GC-MS, at different incubation temperatures (a) and times (b).

To support those visual conclusions, water standards of 100, 500, 1000, 5000 and 10000 ng in 2 mL or 10 mL of distilled water were compared for peak size resolution. An example of the results obtained for ETBE and ethylbenzene are shown in **Figure 3**. The results indicated that the peak size of FO was higher in 2 mL standards, but that of BTEX was higher in 10 mL standards (6-24% higher). However, this last difference was only significant for toluene, ethylbenzene and *m/p*-xylene. According to the analytical results, the increase in the analytical signal was not as significant as to omit the visual conclusions of a better agitation with 2 mL. Therefore, a water volume of 2 mL for aqueous samples and soil slurries was used for HS analysis.

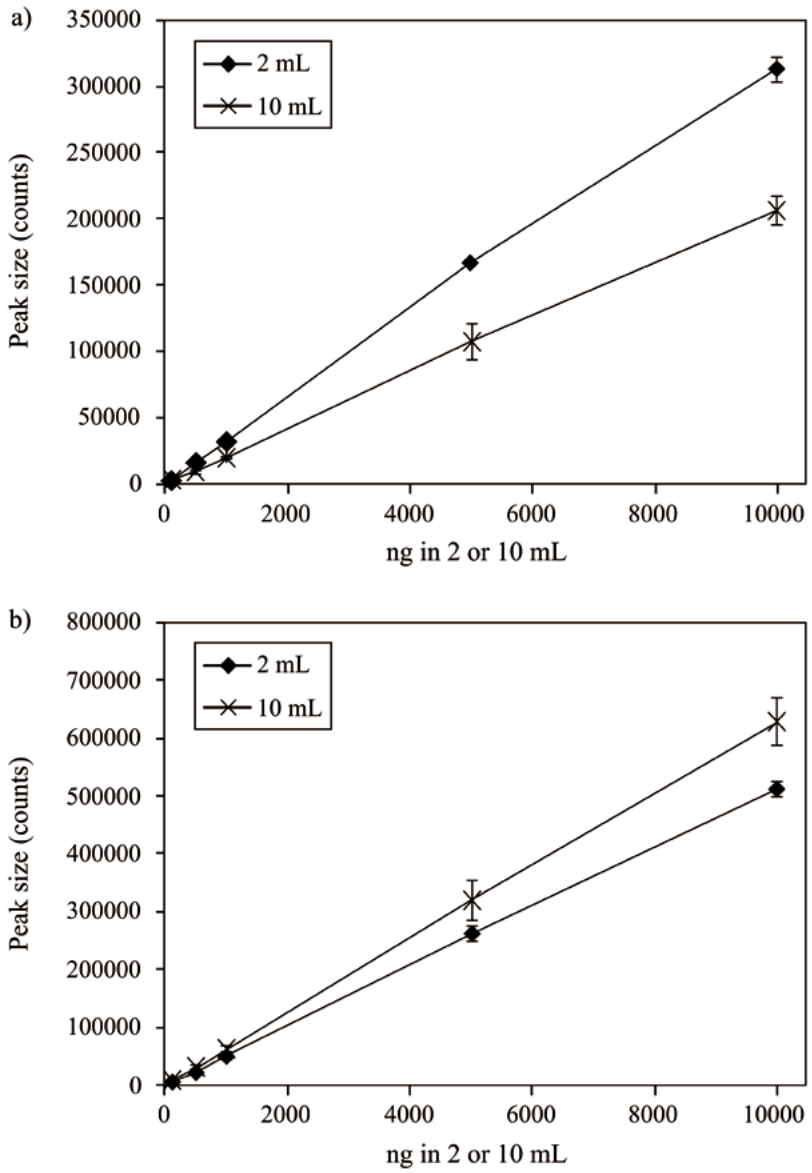

Figure 3. Examples of peak sizes of ETBE (a) and ethylbenzene (b) resulting from HS-GC-MS analysis of 2 mL and 10 mL standards.

Agitation of the sample during HS analysis is very important since it reduces the time required to reach equilibrium by enhancing the diffusion of analytes towards the headspace (Flórez Menéndez et al. 2000). By direct observation, with a speed lower than 500 rpm, water samples, and especially, soil slurries did not agitate properly. At more than 700 rpm, the sample was over-agitated and released drops on the VOA vial, over the liquid or slurry surface. The peak sizes of individual FO and BTEX were slightly higher with 700 rpm than with 500 rpm, but the difference between those agitation speeds was not significant (8-14% difference) (data not shown). Therefore, the agitation speed was fixed at 500 rpm, in order to assure the proper and homogeneous agitation of the water and soil samples.

Thus, the final parameters used for HS extraction of FO and BTEX from water and soil samples are summarized in **Table 1**.

3.1.2. HS analysis validation for soil samples

The principal limitation of HS analysis is the matrix effect, which could be corrected by using surrogate standards (fluorobenzene, in this case). **Figure 4** represents the recovery of individual FO and BTEX from A_{Camb} (**Figure 4a**) and B_{Camb} (**Figure 4b**) spiked with 1000 g kg^{-1}, without and with the surrogate correction.

The use of surrogate significantly increased the FO and BTEX recovery, especially in A_{Camb}: in A_{Camb} the recovery increased from 20-40% without surrogate, to 80-100% with the addition of surrogate; in B_{Camb}, it increased from 70-90% to 80-100%. The principal difference between the soil samples is the organic carbon content (42.6 and 3.3 g kg^{-1} for A_{Camb} and B_{Camb}, respectively). The presence of organic matter in A_{Camb} provoked a stronger sorption on FO and BTEX, than inorganic soil components (clays, oxides and oxihydroxides of iron and aluminium, etc.) in B_{Camb} (Balseiro-Romero and Monterroso 2013). Therefore, surrogates should be used while HS-GC-MS analyzing solid samples, especially if they are expected to exert a strong sorption on analytes.

Table 1. Optimized values of the most important parameters in HS extraction of FO and BTEX

Extraction parameter	Optimized value
Extraction temperature	80 ºC
Extraction time	15 min
Sample size of aqueous samples	2 mL
Sample size of soil samples	Slurry of 1g of soil : 2mL of water
Agitation speed	500 rpm

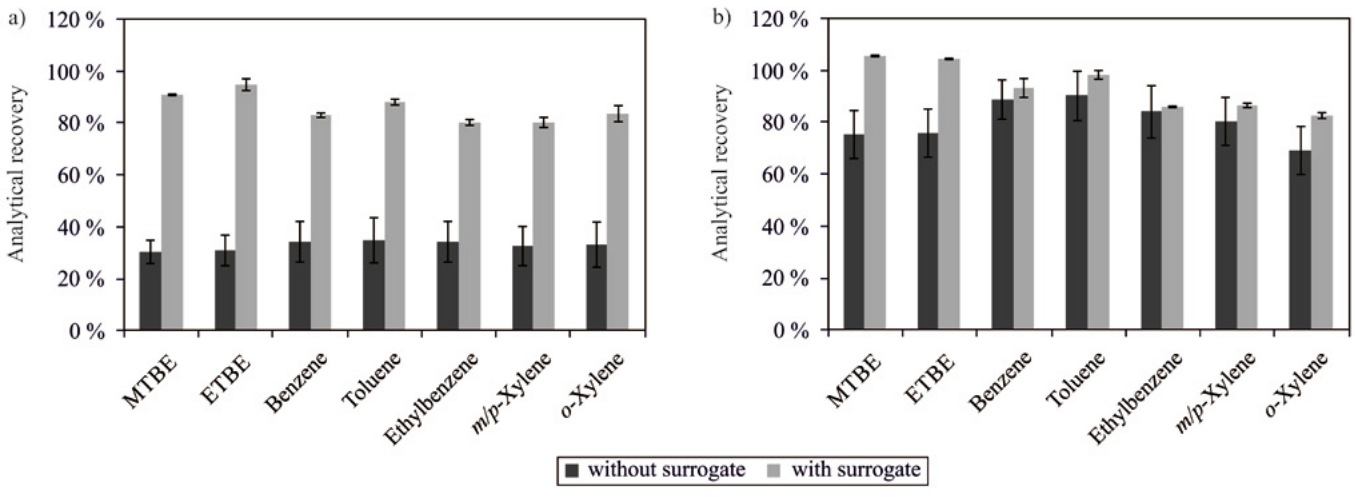

Figure 4. Analytical recoveries of individual FO and BTEX from A_{Camb} (a) and B_{Camb} (b) spiked with 1000 µg kg^{-1} and analyzed by HS-GC-MS without and with the addition of surrogate (fluorobenzene, 5000 µg kg^{-1}).

3.1.3. Analytical performance characteristics of HS-GC-MS

The chromatographic separation of FO and BTEX was simple, considering the small amount of compounds to analyze, their relatively similar properties (volatility, chemical structure) and the injection mode: the HS gas injection or fiber injection generates less peak interferences and therefore higher peak resolution than liquid injection with solvents. Furthermore, based on that high resolution, the mass spectrometer (MS) operated in full scan mode, which also simplifies the GC-MS method.

When the previous extraction step is HS, following the manufacturer´s indications, the GC-MS conditions are those summarized in **Table 2**. An example of a resulting chromatogram is represented in **Figure 5**.

This method could be operated in splitless mode, if more analytical signal was needed. With these conditions and the properties of the column, *m*- and *p*- xylene were hardly separated (they are isomers, and have very similar properties). Therefore, they were quantified as a single peak.

Table 2. Optimized GC-MS conditions for FO and BTEX analysis after HS extraction

GS-MS condition	Optimum value
HS volume injected	1 mL
Injector temperature	250 ºC
Injection mode	1/10 split
Column oven temperature pattern	35 ºC (held for 5 min), 10 ºC min^{-1} up to 80 ºC and 25 ºC min^{-1} up to 200 ºC (held for 0.7 min)
Carrier gas flow	Helium at 1 mL min^{-1}
MS ionization mode	Electron impact
MS ion trap temperature	220 ºC

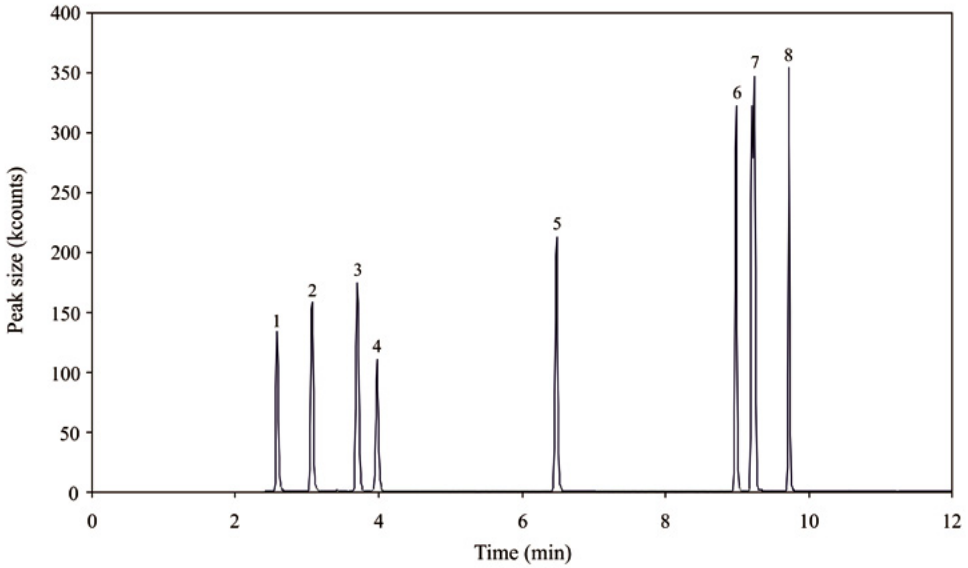

Figure 5. Example of a HS-GC-MS chromatogram of a 5000 µg L^{-1} water standard. The peaks correspond to MTBE (1), ETBE (2), benzene (3), fluorobenzene (4), toluene (5), ethylbenzene (6), *m/p*-xylene (7) and *o*-xylene (8).

The analytical performance characteristics of HS-GC-MS method for VFOC analysis are summarized in **Table 3**.

3.2. FO and BTEX HS-SPME-GC-MS analysis optimization

3.2.1. Optimization of HS-SPME parameters

The optimized parameters used in HS analysis can be used in HS-SPME. The main difference is the incubation time. In this case, the equilibrium takes place between the sample and HS, and then between the HS and the fiber, and higher incubation times should be used.

Indeed, several incubation times were tested (15, 20 and 30 min) (**Figure 6**). Comparable analytical signals were obtained for MTBE and ETBE at all incubation times. However, 30 min of incubation appeared necessary to reach a higher peak size of BTEX compounds.

Table 3. Analytical performance characteristics of HS-GC-MS analysis of FO and BTEX

Contaminant	LOD (µg L^{-1})	LOQ (µg L^{-1})	Linear range (µg L^{-1})	R^2
MTBE	4.6	6.7	15000	0.994
ETBE	1.9	3.4	15000	0.997
Benzene	3.1	7.0	15000	0.994
Toluene	9.8	20.9	15000	0.993
Ethylbenzene	3.7	10.8	15000	0.996
m/p-Xylene	12.7	29.7	15000	0.996
o-Xylene	11.3	26.2	15000	0.996

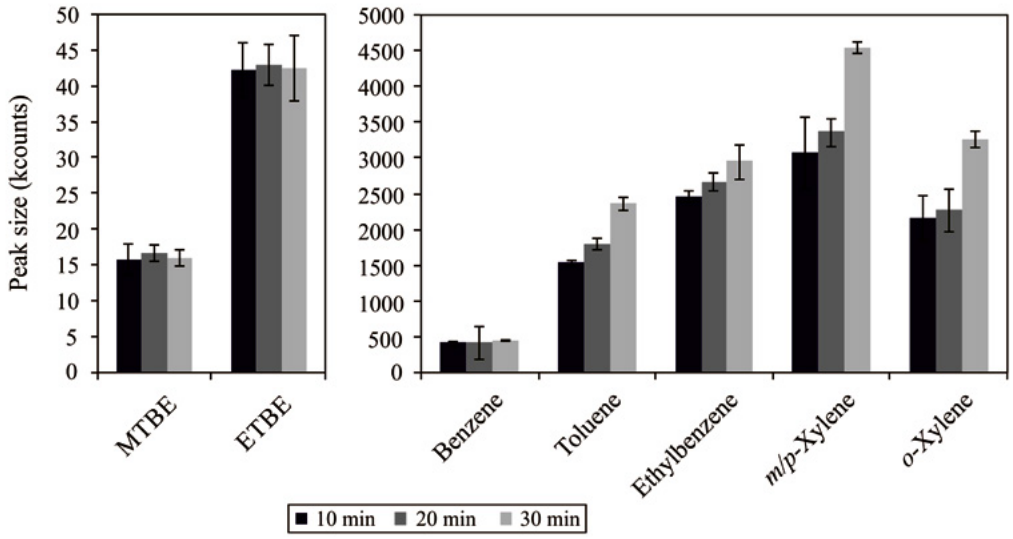

Figure 6. Peak sizes of individual FO and BTEX in 500 µg L^{-1} water standards analyzed by HS-SPME-GC-MS, at different incubation times.

Therefore, the final parameters used for HS-SPME analysis of water and/or soil samples are summarized in **Table 4**.

3.2.2. HS-SPME analysis validation for soil samples

In HS-SPME analysis, as for for HS analysis, matrix effect should be corrected with surrogate standards in order to accurately quantify the soil concentration. **Figure 7** represents the recovery of individual FO and BTEX from A_{Camb} (**Figure 7a**) and B_{Camb} (**Figure 7b**) spiked with 1000 µg kg^{-1}, without and with the surrogate correction.

The use of surrogate was necessary to reach analytical recoveries of up to 100% in both soil samples, and correct the matrix effect.

Table 4. Optimized values of the most important parameters in HS-SPME extraction of FO and BTEX

Extraction parameter	Optimized value
Extraction temperature	80 ºC
Pre-heating time	5 min
Extraction time	30 min
Desorption temperature	300 ºC
Desorption time	5 min
Bakeout temperature	280 ºC
Bakeout time	10 min
Sample size of aqueous samples	2 mL
Sample size of soil samples	Slurry of 1g of soil:2mL of water
Agitation speed	500 rpm

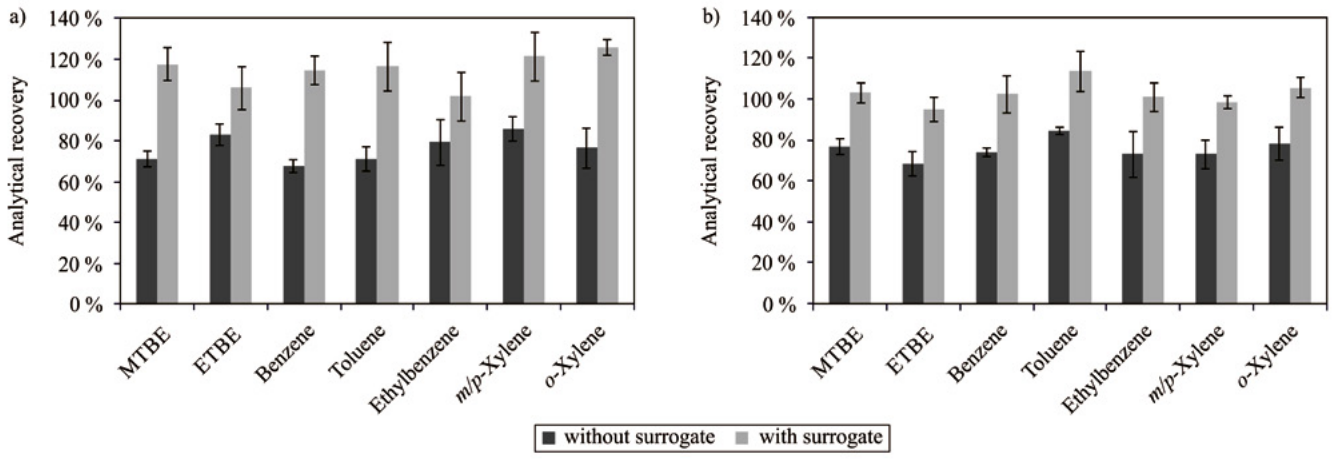

Figure 7. Analytical recoveries of individual FO and BTEX from A_{Camb} (a) and B_{Camb} (b) spiked with 1000 µg kg^{-1} and analyzed by HS-SPME-GC-MS without and with the addition of surrogate (fluorobenzene, 5000 µg kg^{-1}).

3.2.3. Analytical performance characteristics of HS-SPME-GC-MS

When the previous extraction step is HS-SPME, the GC-MS conditions are practically the same as for HS, but the main difference is the injector temperature (**Table 5**). Since the fiber desorption takes place in the injector, the desorption temperature is that defined by the manufacturer, in this case 300 ºC. An example of chromatogram is represented in **Figure 8**.

According to **Figure 8**, the sensitivity of the HS-SPME method is very different for the individual contaminants, contrasting with that of the HS method (**Figure 5**), probably due to the different affinity of the contaminants for the SPME fiber. In addition, the peaks appeared with a tail, probably due to a slow desorption from the fiber. Therefore, quantification was carried out with the peak height instead of with the peak area, as in HS-GC-MS.

Table 5. Optimized GC-MS conditions for FO and BTEX analysis after HS-SPME extraction

GS-MS condition	Optimum value
Injector (desorption) temperature	300 ºC
Injection mode	1/10 split
Column oven temperature pattern	35 ºC (held for 5 min), 10 ºC min^{-1} up to 80 ºC and 25 ºC min^{-1} up to 200 ºC (held for 0.7 min)
Carrier gas flow	Helium at 1 mL min^{-1}
MS ionization mode	Electron impact
MS ion trap temperature	220 ºC

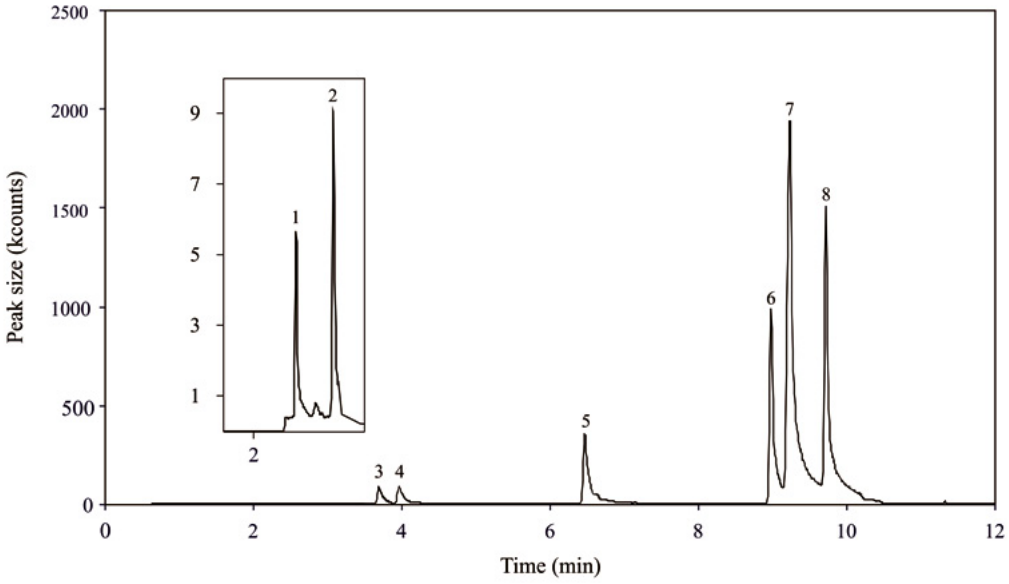

Figure 8. Example of a HS-SPME-GC-MS chromatogram of a 2500 µg L^{-1} water standard. The peaks correspond to MTBE (1), ETBE (2), benzene (3), fluorobenzene (4), toluene (5), ethylbenzene (6), *m/p*-xylene (7) and *o*-xylene (8).

The analytical performance characteristics of HS-SPME-GC-MS method are summarized in **Table 6**. Detection and quantification limits, and linearity were calculated as for HS-GC-MS method.

Table 6. Analytical performance characteristics of HS-SPME-GC-MS analysis of FO and BTEX

Contaminant	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	Linear range ($\mu g\ L^{-1}$)	R^2
MTBE	1.9	3.3	2500	0.990
ETBE	0.5	0.9	2500	0.981
Benzene	0.5	1.0	2500	0.996
Toluene	0.8	1.9	2500	0.991
Ethylbenzene	1.1	3.3	2500	0.991
m/p-Xylene	0.9	2.6	2500	0.993
o-Xylene	2.6	7.3	2500	0.994

4. Conclusions

The use of HS or HS-SPME in FO and BTEX GC-MS analysis will highly depend on the concentration of the samples. When this concentration is unknown, HS should be used as screening method, since it has a longer linear range (until 30 mg Kg^{-1} or 15 mg L^{-1}). If the analytical response of the contaminants is under or near the HS quantification limit, HS-SPME should be used. In our study this last method amplified the analytical response of HS more than 20 times, and its detection and quantification limits were about an order of magnitude under HS values.

The use of surrogate standards in soil analysis was essential to correct the matrix effect and to properly quantify soil concentration.

The HS and HS-SPME analysis methods developed in this study resulted in sensitive and accurate procedures to identify and quantify volatile organics (VFOC), MTBE, ETBE and BTEX, in environmental samples. Therefore, they can be used for the characterization of the contamination in a real fuel spill episode, over a wide range of contaminant concentrations and for water and soil samples with different organic matter contents.

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